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Superior aqueous-phase catalytic hydrogenation activity of palladium modified with nitrogen-containing ligands compared with the TPPTS benchmark modifier in micellar nanoreactors

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ABSTRACT

Exceptionally high catalytic activities (TOF = 110,000 h^{-1}) have been achieved by water-dispersible palladium(0) nanoparticle catalysts stabilized by water-soluble nitrogen-containing ligands in the hydrogenation of renewable polyunsaturated methyl esters of soybean oil (MESBO) to their monounsaturated counterparts in aqueous/organic micellar systems. Palladium(II) chloride catalyst precursors exhibited a superior aqueous-phase catalytic activity with various nitrogen-containing ligands inter alia bathophenanthrolinedisulfonic acid disodium salt [(BPhDS) (TOF = 71,000 h^{-1})], diethylenetriaminepentakis (methylphosphonic acid) (TOF = 68,000 h^{-1}), ethylenediaminetetraacetic acid tetrasodium salt (TOF = 50,000 h^{-1}) compared with the TPPTS benchmark ligand modifier (TOF = 34,000 h^{-1}) in this environmentally friendly biphasic catalytic hydrogenation reaction. Mercury poisoning experiments of preformed Pd/BPhDS catalysts proved the heterogeneous nature of this catalytic hydrogenation system. Dynamic light scattering experiments evidenced the presence of micellar nanoreactors with in situ prepared $[Pd(OAc)_2]_3$/BPhDS catalyst possessing an average hydrodynamic radius of 36 nm and with preformed and recycled $PdCl_2$/BPhDS catalyst with an average hydrodynamic radius of 57 nm. The apparent activation energy of preformed palladium(0) nanoparticle hydrogenation catalysts stabilized by BPhDS in micellar systems was calculated to 23.7 kJ/mol which is of the same order of magnitude as reported earlier for palladium(0) nanoparticles stabilized by dendritic core-multishell architectures. A recycling experiment at 120 °C showed that the activity of palladium(0) nanoparticle catalyst stabilized by BPhDS in micellar systems in aqueous media remained high in a consecutive run indicating a stable palladium(0) catalytic nanoparticle system which is remarkable when one considers that transition metal(0) catalytic nanoparticles are usually applied at much lower temperatures due to their lower stabilities.

1. Introduction

Nowadays, there is increasing interest in catalysis in aqueous/organic two-phase systems employing water-soluble transition metal catalytic complexes because aqueous media facilitate recovery and recycling of the catalyst and this mode of heterogenization of homogeneous catalysis has been further stimulated by increasing environmental constraints because catalysis in aqueous media obviates the need for conventional organic toxic solvents and water is a non-toxic, non-inflammable, safe, inexpensive, abundantly available and a green solvent [1–7]. Moreover, the large heat capacity of water makes it an excellent medium to perform exothermic reactions such as hydrogenation reactions more safe and selective which is especially important in industrial large scale exothermic catalytic processes. Water-soluble transition metal catalytic complexes modified with a broad spectrum of water-soluble ligands have found numerous laboratory scale applications in many different types of catalytic reactions and water-soluble Rh/TPPTS catalytic complexes [TPPTS = $P(C_6H_4$-*m*-$SO_3Na)_3$] have found important industrial applications such as in the Ruhrchemie/Rhône-Poulenc process for the hydroformylation of lower olefins in aqueous/organic two-phase systems [1–3].

Water-soluble Pd/TPPTS complexes are very versatile catalysts for a broad spectrum of different types of aqueous-phase catalytic reactions [1–3], e.g. carbonylation reactions [8–15] and Pd/TPPTS catalytic complexes have been also applied in hydrogenation reactions of citral [16], crotonaldehyde [17], cinnamaldehyde [17] and aromatic nitrocompounds [18] in aqueous media. The vast majority of water-soluble ligands to modify transition metal complexes are phosphine ligands [1–3] and have been applied in almost the whole spectrum of aqueous-phase organometallic catalysis. In sharp contrast, only a little attention have received

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water-soluble nitrogen-containing ligands which combine several advantages such as: (i) higher hydrophilicity in general compared with their phosphorous-containing counterparts [19,20], (ii) lower price which is in accordance with the quest to develop "*cheap metal and ligands for noble tasks*" [21], and (iii) their higher stability compared with phosphine ligands. Water-soluble nitrogen-containing ligands, have not been extensively used for aqueous-phase catalytic applications except in the field of palladium/N-ligands-catalyzed oxidation reactions in water [22–27]. To our knowledge, the only example of an aqueous-phase homogeneous palladium/N-ligand-catalyzed hydrogenation reaction makes use of water-soluble palladium complexes containing nitrogen ligands derived from carbohydrates [28] and there is no study on the comparison of catalytic activity of water-soluble transition metal catalytic complexes modified with phosphine ligands such as the TPPTS benchmark ligand compared with nitrogen-containing ligands in hydrogenation reactions in aqueous/organic two-phase systems. We here report an investigation on the catalytic activity of aqueous-phase palladium catalysts containing nitrogen ligands compared with Pd/TPPTS catalysts in the aqueous/organic micellar selective hydrogenation of renewable methyl esters of soybean oil to obtain upgraded biodiesel fuel with improved oxidative stability, energy and environmental performance at a low pour point.

2. Experimental

2.1. Materials

Hydrogen (quality 5.0) was purchased from Air Liquide Hellas A.E.B.A. (Athens) and was used without further purification. Distilled demineralized water was deoxygenated in an ultrasound bath under high vacuum for 2 h. During the deoxygenation the flask was disconnected from the vacuum, and the aqueous solvent was saturated with argon; this procedure was repeated several times. Soybean oil was purchased from MP Biomedicals and was used without any further purification. $Pd(MeCN)_2(O_3STol)_2$ was prepared according to the procedure of Drent et al. [29]. $Pd(OAc)_2$ and $Pd(acac)_2$ were purchased from Alfa Aesar and $PdCl_2$ from Fluka. TPPTS was prepared according to literature procedures [30–37] and isolated with purity higher than 98%. Bathophenanthrolinedisulfonic acid disodium salt (BPhDS) was obtained from Acros Organics; bathocuproinedisulfonic acid disodium salt (BCDS) and ethylenediaminetetraacetic acid tetrasodium salt ($EDTANa_4 \cdot H_2O$) were purchased from Alfa Aesar; diethylenetriaminepentakis(methylphosphonic acid) (DTPPA), nitrilotris(methylphosphonic acid) (NTPA), *trans*-1,2-diaminocyclohexane-N,N,N′,N′-tetraacetic acid (CyDTA) and diethylenetriaminepentaacetic acid pentasodium salt ($DTPANa_5$) were purchased from Fluka; ethylenediaminetetraacetic acid (EDTA) was purchased from Sigma; sulfanilic acid sodium salt (SANa) and 2,2′-biquinoline-4,4′-dicarboxylic acid dipotassium salt (BQC) were obtained from Aldrich. All nitrogen containing ligands mentioned were used without any further purification. Mercury was purchased from Alfa Aesar.

2.2. Transesterification reaction of soybean oil with methanol

A 1000-ml, three-necked, round-bottom flask, equipped with a mechanical stirrer, a thermometer and a condenser was charged with 315.0 g of soybean oil and a solution of 185.6 g methanol containing 3.15 g of NaOH. The mixture was stirred at 55 °C for 70 min. The course of the reaction was followed by thin layer chromatography. The reaction mixture was then cooled and further stirred for 5.5 h at room temperature. After phase separation resulted in the isolation of the methyl esters of soybean oil (MESBO) and the glycerol. The glycerol phase (bottom layer) was removed and kept in a separate container. The MESBO phase (top layer) was washed with distilled water several times (pH 7.0), dried over Na_2SO_4 to obtain 250.4 g of crude MESBO mixture which was used as starting material in the hydrogenation reaction without any further purification. Methyl esters compositions of soybean oil was determined by gas chromatography (vide infra) and are given in Tables 1–3.

2.3. Catalytic hydrogenation experiments

In a typical hydrogenation reaction of MESBO: 2.65 mg (0.005 mmol) $Pd(MeCN)_2(O_3STol)_2$ and 9.3 mg (0.015 mmol) TPPTS (TPPTS/Pd molar ratio = 3) were dissolved under argon in 15 ml deaerated demineralized water under stirring. This aqueous catalyst solution, having a palladium concentration of 35 ppm, with 10.12 g (50 mmol of C=C units) of MESBO mixture which results a two-phase system with a volume ratio of aqueous/organic phase = 15/11.2, were charged into an Autoclave Engineers autoclave (100 ml) which was previously evacuated and filled with argon. In the reaction mixture the molar ratio of C=C units/Pd was 10 000. After a number of pressurizing–depressurizing cycles with hydrogen to remove last traces of air oxygen, the autoclave was pressurized and contents were heated with stirring (stirring rate = 740 rpm). The heating time to reach a reaction temperature of 120 °C was 4 min. At the reaction temperature of 120 °C the hydrogen partial pressure was 20 bar and the reaction time 5 min. After the reaction the autoclave was cooled (within 3 min) to room temperature, vented of hydrogen and the reaction mixture removed. The upper organic layer was easily separated from the lower aqueous layer containing the catalyst and dried over sodium sulfate. The organic layer containing the products was analyzed by gas chromatography (GC) after addition of methyl heptadecanoate as standard.

2.4. Analysis of TPPTS, MESBO and the products of the hydrogenation reaction

The purity of the TPPTS ligand was determined by quantitative $^{31}P\{^1H\}$NMR analysis in D_2O at 25 °C. δ TPPTS = −5.4 ppm. $^{31}P\{^1H\}$NMR spectra (121 MHz, referenced to external 85% H_3PO_4) were recordered on a Varian Unity Plus 300/54 spectrometer. The various polyunsaturated, monounsaturated and saturated FAME isomers contained in the starting material MESBO and the hydrogenation products were identified by comparison of GC and gas chromatography/mass spectrometry (GC/MS) analytic data with data for authentic samples. GC/MS was measured on a Varian Star 3400CX GC coupled with a Varian Saturn 2000 ion trap MS. The GC was equipped with a flame ionization detector (FID) and a SP-2560 capillary column (100 m × 0.25 mm i.d. × 0.2 μm film thickness) which was purchased from Supelco (Athens, Greece). The SP-2560 capillary column is one of the two columns applied in the approved American Oil Chemists' Society (AOCS) official method Ce 1 h–05 for the determination of *cis*-, *trans*-, saturated, monounsaturated and polyunsaturated fatty acids in vegetable or non-ruminant animal oils and fats by capillary GLC method [38]. Carrier gas was He at 230 kPa. The oven temperature was initially at 170 °C for 0 min and then increased to 220 °C at 1 °C/min. The injector and detector temperatures were set at 220 °C and 230 °C, respectively. The GC analyses were run on a Shimadzu GC-14B equipped with a FID detector and a HP-Innowax capillary column (30 m × 0.251 mm i.d. × 0.50 μm film thickness) which was purchased from Agilent Technologies. Carrier gas was N_2 at 235 kPa. The oven temperature was initially at 150 °C for 5 min and then increased to 240 °C at 3 °C/min. The injector and detector temperatures both were set at 240 °C.

Table 1
Effect of temperature, hydrogen pressure, C=C/Pd molar ratio and of palladium catalyst precursors on the Pd/TPPTS-catalyzed partial hydrogenation of MESBO in aqueous/organic two-phase systems.[a]

Entry	Starting material	Catalyst precursor	C=C/Pd molar ratio	T (°C)	P_{H_2} (bar)	C18:3 (total) (mol%)	C18:2 (total) (mol%)	C18:1 (total) (mol%)	MS (mol%)	TOF[b] (h^{-1})
–	MESBO 1[c]	–	–	–	–	3.8[d]	46.4[e]	43.2[f]	6.6	–
1/1	MESBO 1	$Pd(MeCN)_2(O_3STol)_2$	3000	90	30	0.0	8.6	71.9	19.5	15,000
1/2	MESBO 1	$Pd(MeCN)_2(O_3STol)_2$	3000	100	30	0.0	4.7	71.0	24.3	16,400
1/3	MESBO 1	$Pd(MeCN)_2(O_3STol)_2$	3000	110	30	0.7	3.3	67.8	28.2	16,700
1/4	MESBO 1	$Pd(MeCN)_2(O_3STol)_2$	3000	120	30	0.0	2.8	73.5	23.7	17,100
1/5	MESBO 1	$Pd(MeCN)_2(O_3STol)_2$	3000	130	30	0.0	3.8	63.8	32.4	16,700
1/6	MESBO 1	$Pd(MeCN)_2(O_3STol)_2$	3000	130	50	0.0	4.2	29.9	66.0	42,800
1/7	MESBO 1	$Pd(MeCN)_2(O_3STol)_2$	1500	120	30	0.0	50.6	27.9	20.5	3300
1/8	MESBO 1	$Pd(MeCN)_2(O_3STol)_2$	5000	120	30	0.0	4.1	77.8	18.1	27,700
1/9	MESBO 1	$Pd(MeCN)_2(O_3STol)_2$	10,000	120	20	1.1	5.6	72.6	20.8	52,300
1/10	MESBO 1	$Pd(OAc)_2$	10,000	120	20	0.9	8.5	81.4	9.3	49,000
1/11	MESBO 1	$PdCl_2$	10,000	120	20	1.2	20.2	70.0	8.5	34,500
1/12	MESBO 1	$Pd(acac)_2$	10,000	120	20	3.4	35.3	54.0	7.2	13,700

[a] Reaction conditions: t = 5 min; 0.005 mmol of palladium catalyst precursor; 9.3 mg (0.015 mmol) TPPTS (P/Pd molar ratio = 3); 15 ml deaerated demineralized water, [Pd] = 35 ppm. Addition of 10.12 g (50 mmol of C=C units) of MESBO 1 mixture (C=C units/Pd molar ratio = 10,000) to the aqueous catalyst solution results a two-phase system with a volume ratio of aqueous/organic phase = 1.33. Range of the volume ratios of aqueous/organic phase = 1.33–8.89. No addition of organic solvents. Stirring rate = 740 rpm.
[b] Defined as mole of hydrogenated C=C units in the C18:3, C18:2, and C18:1 compounds and the increase in mole of MS in the starting material MESBO 1 mixture and all other regioisomers formed during the course of the reaction per mole of palladium per hour.
[c] MESBO 1 except of α-MLN, ML, MO and MS further contained 20.7% of methyl palmitate (MP, C16:0) which was ignored in the experiments.
[d] Methyl α-linolenate (α-MLN), C18:3 (9c, 12c, 15c).
[e] Methyl linoleate (ML), C18:2 (9c, 12c).
[f] Methyl oleate (MO), C18:1 (9c).

2.5. Dynamic light scattering

Measurements were conducted with a Series 4700 Malvern system composed of a PCS5101 goniometer with a PCS stepper motor controller, a Cyonics variable power Ar^+ laser, operating at 488 nm, a PCS8 temperature control unit, a RR98 pump/filtering unit and a 192 channel correlator for the accumulation of the data. The correlation functions were analyzed by the cumulant method and CONTIN software. Measurements were carried out at 90°. The angular dependence of the ratio Γ/q^2, where Γ is the decay rate of the correlation function and q is the scattering vector, was not very important for the micellar solutions, due to their large sizes. Apparent translational diffusion coefficients at zero concentration, $D_{o,app}$ were measured using the equation: $D_{app} = D_{o,app}(1 + k_D c)$ (2); where k_D is the coefficient of the concentration dependence of the diffusion coefficient. Apparent hydrodynamic radii at infinite dilutions, R_h, were calculated by aid of the Stokes–Einstein equation: $R_h = kT/6\pi\eta_s D_{o,app}$ (3); where k is the Boltzmann's constant, T the absolute temperature and η_s the viscosity of the solvent.

Table 2
Effect of palladium catalyst precursors modified with various water-soluble nitrogen-containing ligands on the partial hydrogenation of MESBO in aqueous/organic two-phase systems.[a]

Entry	Starting material	Catalyst precursor	Water-soluble ligand	C=C/Pd molar ratio	C18:3 (total) (mol%)	C18:2 (total) (mol%)	C18:1 (total) (mol%)	MS (mol%)	TOF[b] (h^{-1})
–	MESBO 2[c]		–	–	10.3[d]	57.5[e]	27.3[f]	4.9	–
2/1	MESBO 2	$PdCl_2$	BPhDS	10,000	0.0	8.4	78.4	13.3	71,300
2/2	MESBO 2	$Pd(OAc)_2$	BPhDS	10,000	0.6	15.5	78.0	5.9	62,000
2/3	MESBO 2	$Pd(acac)_2$	BPhDS	10,000	0.3	26.5	67.6	5.6	49,200
2/4	MESBO 2	$Pd(MeCN)_2(O_3STol)_2$	BPhDS	10,000	0.0	30.0	64.6	5.4	45,300
2/5	MESBO 2	$PdCl_2$	DTPPA	10,000	0.0	11.2	79.8	9.0	68,000
2/6	MESBO 2	$PdCl_2$	BCDS	10,000	0.0	15.3	78.8	5.9	63,000
2/7	MESBO 2	$PdCl_2$	NTPA	10,000	1.6	16.9	74.6	6.9	59,100
2/8	MESBO 2	$PdCl_2$	CyDTA	10,000	0.9	21.7	69.3	8.1	54,200
2/9	MESBO 2	$PdCl_2$	$EDTANa_4$	10,000	0.2	25.3	68.4	6.1	50,700
2/10	MESBO 2	$PdCl_2$	EDTA	10,000	0.5	26.9	65.0	7.5	48,400
2/11	MESBO 2	$PdCl_2$	$DTPANa_5$	10,000	1.7	29.3	62.4	6.6	44,100
2/12	MESBO 2	$PdCl_2$	SANa	10,000	1.4	30.2	62.5	5.8	43,400
2/13	MESBO 2	$PdCl_2$	BQC	10,000	1.2	33.6	59.6	5.6	39,700
2/14	MESBO 2	$PdCl_2$	BPhDS	15,000	0.6	40.2	54.5	4.7	110,000

[a] Reaction conditions: T = 120 °C; $P_{H_2} = 20$ bar; t = 5 min; except entry 2/14, t = 3 min; 0.005 mmol of palladium catalyst precursor; 0.005 mmol of water-soluble nitrogen-containing (N-ligand/Pd molar ratio = 1); except entry 2/10, EDTA/Pd molar ratio = 0.3; 15 ml deaerated demineralized water; [Pd] = 35 ppm. Addition of 9.23 g (50 mmol of C=C units) of MESBO 2 mixture (C=C units/Pd molar ratio = 10,000) to the aqueous catalyst solution results a two-phase system with a volume ratio of aqueous/organic phase = 1.46. Range of the volume ratios of aqueous/organic phase = 0.97–1.46. No addition of organic solvents. Stirring rate = 740 rpm.
[b] Defined as mole of hydrogenated C=C units in the C18:3, C18:2, and C18:1 compounds and the increase in mole of MS in the starting material MESBO 1 mixture and all other regioisomers formed during the course of the reaction per mole of palladium per hour.
[c] MESBO 2 except of α-MLN, ML, MO and MS further contained 10.4% of methyl palmitate (MP, C16:0) which was ignored in the experiments.
[d] Methyl α-linolenate (α-MLN), C18:3 (9c, 12c, 15c).
[e] Methyl linoleate (ML), C18:2 (9c, 12c).
[f] Methyl oleate (MO), C18:1 (9c).

Table 3
Recycling of water-dispersible palladium(0) nanoparticle catalysts stabilized by BPhDS ligands, effect of temperature and the mercury poisoning test in the partial hydrogenation of MESBO in aqueous/organic micellar systems.[a]

Entry	Starting material	Catalyst precursor	C=C/P molar ratio	T (°C)	C18:3(total) (mol%)	C18:2 (total) (mol%)	C18:1 (total) (mol%)	MS (mol%)	TOF[b] (h^{-1})
–	MESBO 3[c]				7.6[d]	60.0[e]	28.1[f]	4.3	–
3/1	MESBO 3	Preformed Pd/BPhDS[h]	12,000	120	4.1	49.0	42.3	4.6	5400
3/2[g]	MESBO 3	Recycled catalyst[h]	12,000	120	4.5	48.5	42.4	4.6	5480
–	MESBO 4	–	–	–	8.0	60.5	27.3	4.2	–
3/3	MESBO 4	Preformed Pd/BPhDS[i]	2000	100	0.0	25.6	65.7	8.7	2100
3/4	MESBO 4	Preformed Pd/BPhDS[i]	2000	110	0.0	26.4	51.6	22.0	2500
3/5	MESBO 4	Preformed Pd/BPhDS[i]	2000	120	0.0	17.1	73.0	9.9	3100
3/6	MESBO 4	Preformed Pd/BPhDS[i]/Hg[j]	2000	120	7.9	59.6	27.9	4.6	60

[a] Reaction conditions: $P_{H_2} = 20$ bar; t = 20 min; 15 ml deaerated demineralized water; [Pd] = 35 ppm. Addition of 13.01 g (60 mmol of C=C units) of MESBO 3 mixture to the aqueous catalyst solution results a two-phase system with a volume ratio of aqueous/organic phase = 1.04 for the entries 3/1 and 3/2. Addition of 2.15 g (10 mmol of C=C units) of MESBO 4 mixture to the aqueous catalyst solution results a biphasic system with a volume ratio of aqueous/organic phase = 6.27. The pH value of the aqueous catalyst solution after the reaction of entries 3/3–3/6 was 4.42–4.86. All hydrogenation experiments of this table (entries 3/1–3/6) were carried out in an *Autoclave Engineers* autoclave (100 ml) equipped with a stir bar driven by an IKA magnetic stirrer (poorer mixing) because its own MagneDrive III agitator system was out of order. The colour of the aqueous catalyst phase was black–brown in all hydrogenation experiments (entries 3/1–3/6).

[b] Defined as mole of hydrogenated C=C units in the C18:3, C18:2, and C18:1 compounds and the increase in mole of MS in the starting material MESBO 3 mixture and all other regioisomers formed during the course of the reaction per mole of palladium per hour.

[c] MESBO 3 except of α-MLN, ML, MO and MS further contained 9.8% of methyl palmitate (MP, C16:0) which was ignored in the experiments.

[d] Methyl α-linolenate (α-MLN), C18:3 (9c, 12c, 15c).

[e] Methyl linoleate (ML), C18:2 (9c, 12c).

[f] Methyl oleate (MO), C18:1 (9c).

[g] The aqueous catalyst layer (15 ml) of entry 3/1, after separation of the upper organic phase, was re-used with addition of a new portion of 13.01 g (60 mmol C=C units) of MESBO 3.

[h] A minor amount of palladium black was observed after the reaction.

[i] 1.12 mg (0.00166 mmol) $[Pd(OAc)_2]_3$, i.e. 0.005 mmol $Pd(OAc)_2$ and 2.68 mg (0.005 mmol) BPhDS were added to 15 ml of demineralized H_2O and after slight heating for a few minutes the mixture was stirred overnight at room temperature to give a yellow solution. The amount of uncomplexed palladium was then removed by filtration.

[j] Addition of 300.9 mg (1.5 mmol) Hg(0) which is an excess of 300 equiv. over the palladium catalyst.

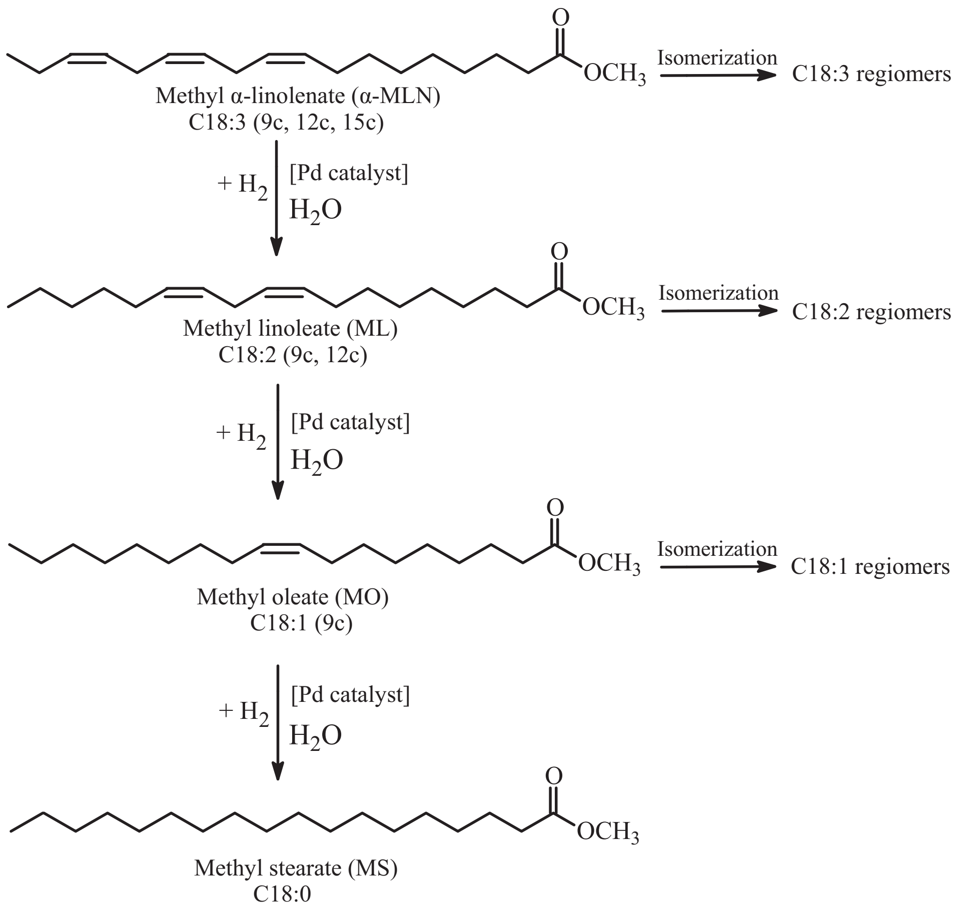
3. Results and discussion

3.1. *Selective hydrogenation of polyunsaturated methyl esters of vegetable oils to their monounsaturated (C18:1) counterparts*

We and others previously reported that partial hydrogenation processes of polyunsaturated alkyl esters of vegetable oils into their monounsaturated counterparts (Scheme 1) without increasing the saturated part are of great interest in the fields of production of high quality 1st generation biodiesel fuel and of biolubricants in terms of improved oxidative stability, energy and environmental performance at a low pour point [39–50]. Moreover, partial hydrogenation reactions possess a great potential to produce 2nd generation biodiesel from polyunsaturated fatty acid methyl esters (FAME) of alternative, non-food oil feedstocks which are originally not suitable for biodiesel production or give poor quality biodiesel fuel but combine the advantage that they would not affect food production [42,48].

3.1.1. *Selective hydrogenation of methyl esters of soybean oil (MESBO) catalyzed by Pd/TPPTS complexes in aqueous/organic two-phase systems*

Table 1 presents the activity and selectivity of water-soluble Pd/TPPTS catalytic complexes as a function of temperature, hydrogen partial pressure, C=C/Pd molar ratio and of the palladium catalysts precursors in the hydrogenation of polyunsaturated methyl esters of MESBO to their monounsaturated counterparts (Scheme 1) in aqueous/organic two-phase systems. The catalytic activity in the $Pd(MeCN)_2(O_3STol)_2$/TPPTS-catalyzed biphasic hydrogenation of MESBO increases with increasing temperature from 90 up to 130 °C to give TOF values from 15,000 up to 16,700 h^{-1} and the selectivities to C18:1 ester regioisomers decreased with increasing temperature from 71.9 to 63.8 mol% at a palladium concentration of only 35 ppm in the aqueous medium (Table 1, entries 1/1–1/5). The effect of hydrogen pressure in the partial hydrogenation of MESBO catalyzed by water-soluble $Pd(MeCN)_2(O_3STol)_2$/TPPTS complexes in aqueous/organic two-phase systems is shown in Table 1 and the catalytic activity increased from TOF = 16,700 h^{-1} to TOF = 42,800 h^{-1} and as expected the selectivity towards the undesired saturated product methyl stearate (MS, Scheme 1) increased to give from 32.4 up to 66.0 mol% MS with increasing pressure from 30 to 50 bar in the aqueous solvent (entries 1/5, 1/6). We have observed a similar behaviour of considerable increase in catalytic activity with increasing pressure above 30 bar in aqueous-phase Rh/TPPTS-catalyzed hydrogenations of polyunsaturated methyl esters of vegetable oils probably due to the lower mass transfer limitations resulting from a better solubilization of the surface active polyunsaturated substrate (with small amounts of lecithin) in the core of micelles containing catalytic active sites. Lecithin which is a natural phospholipid surfactant inherent in several vegetable oils is present in small amounts in our MESBO starting material mixture and therefore micellar catalysis is also operative without any addition of external surfactants in aqueous/organic two-phase systems. To study the dependence of the C=C units/Pd molar ratio on the $Pd(MeCN)_2(O_3STol)_2$/TPPTS-catalyzed catalyzed biphasic partial hydrogenation of MESBO, a series of reactions were carried out by varying the molar ratio of C=C units/Pd over the range of 1500–5000 at 120 °C keeping the hydrogen partial pressure (30 bar), the reaction time (5 min), the molar ratios of TPPTS/Pd (3) and the palladium concentration in water (35 ppm) constant. The catalytic activity considerably increased from TOF = 3300 h^{-1} to TOF = 27,700 h^{-1} and the selectivity towards total C18:1 esters also increased from 27.9 to 77.8 mol% with increasing molar ratios of C=C units/Pd from 1500 to 5000 at a reaction temperature of 120 °C in the $Pd(MeCN)_2(O_3STol)_2$/TPPTS-catalyzed hydrogenation of MESBO in aqueous/organic two-phase systems (Table 1, entries 1/7, 1/4 and 1/8). The highest catalytic activity (TOF = 52,300 h^{-1}) in the Pd/TPPTS-catalyzed hydrogenation of MESBO was achieved with $Pd(MeCN)_2(O_3STol)_2$ catalyst precursors whereas the catalytic activity decreased in the order: $Pd(OAc)_2$ > $PdCl_2$ > $Pd(acac)_2$ precursors to give turnover frequencies of 49,000 h^{-1}, 34,500 h^{-1} and 13,700 h^{-1}, respectively at 120 °C and molar ratios of C=C units/Pd = 10,000 and TPPTS/Pd = 3 under 20 bar hydrogen partial



Scheme 1. Selective hydrogenation of polyunsaturated methyl esters of soybean oil (MESBO) to their monounsaturated (C18:1) counterparts catalyzed by water-soluble palladium catalysts modified with TPPTS and by water-dispersible palladium(0) nanoparticle catalyst stabilized with nitrogen-containing ligands in aqueous/organic micellar systems. The term "regioisomers" refers to all isomers obtained from hydrogenation and/or positional isomerization (along the carbon chain) reactions and all other geometric isomers formed via *cis*/*trans* isomerization reactions.

pressure within 5 min of reaction time and a palladium concentration of 35 ppm in the aqueous medium (Table 1, entries 1/9–1/12). However, the highest selectivity towards C18:1 ester regiomers of 81.4 mol% was obtained with $Pd(OAc)_2$/TPPTS catalysts in the aqueous medium (entry 1/10).

3.1.2. Selective hydrogenation of MESBO catalyzed by water-soluble palladium complexes containing nitrogen ligands in aqueous/organic two-phase systems

Table 2 shows the activity and selectivity of in situ formed water-soluble palladium catalytic systems in the partial hydrogenation of polyunsaturated methyl esters of MESBO to their monounsaturated counterparts as a function of different palladium catalyst precursors and various nitrogen-containing ligands in aqueous/organic two-phase systems. The highest catalytic activity (TOF = 71,300 h^{-1}) and selectivity towards C18:1 ester regioisomers (78.4 mol%) in the partial hydrogenation reaction of MESBO was achieved with $PdCl_2$ catalysts precursors modified with water-soluble bathophenanthrolinedisulfonic acid disodium salt (BPhDS) ligands (Fig. 1) at a molar ratio of C=C units/Pd = 10,000 and BPhDS/Pd = 1, a reaction temperature of 120 °C under 20 bar hydrogen partial pressure within 5 min of reaction time and a palladium concentration of only 35 ppm in the aqueous phase of the biphasic systems (Table 2, entry 2/1). In contrast, the catalytic activity exhibited the $PdCl_2$ catalyst precursor modified with the TPPTS benchmark ligand was much lower (TOF = 34,500 h^{-1}) under the same conditions in this biphasic hydrogenation reaction (Table 1, entry 1/11). In the partial hydrogenation reaction of MESBO in the presence of water-soluble palladium complexes with BPhDS ligands the catalytic activity of palladium precursors decreased in the order: $PdCl_2 > Pd(OAc)_2 > Pd(acac)_2 > Pd(MeCN)_2(O_3STol)_2$ to give TOF's of 71,300 h^{-1}, 62,000 h^{-1}, 49,200 h^{-1} and 45,300 h^{-1}, respectively, in aqueous/organic two-phase systems (Table 2, entries 2/1–2/4). High catalytic activities (TOF = 68,000–63,000 h^{-1}) and high selectivities to C18:1 esters of 79.8–78.8 mol% were exhibited by $PdCl_2$ precursors modified with both diethylenetriaminepentakis(methylphosphonic acid) (DTPPA) and bathocuproinedisulfonic acid disodium salt (BCDS, Fig. 1) ligands in the partial hydrogenation of MESBO at a molar ratio of C=C units/Pd = 10,000 and N-ligand/Pd = 1, a reaction temperature of 120 °C under 20 bar hydrogen partial pressure within 5 min of reaction time in aqueous/organic two-phase systems (Table 2, entries 2/5 and 2/6). The catalytic hydrogenation activity exhibited by $PdCl_2$ catalyst precursors modified with the nitrogen containing water-soluble ligands nitrilotris(methylphosphonic acid) (NTPA), *trans*-1,2-diaminocyclohexane-N,N,N′,N′-tetraacetic acid (CyDTA), ethylenediaminetetraacetic acid tetrasodium salt ($EDTANa_4$) and ethylenediaminetetraacetic acid (EDTA) are in the range of 59,100 and 48,400 TOF's per hour and the selectivities to C18:1 esters of 74.6–65.0 mol% (Table 2, entries 2/7–2/10). In contrast, with the water-soluble nitrogen-containing ligands diethylenetriaminepentaacetic acid pentasodium salt ($DTPANa_5$), sulfanilic acid sodium salt (SANa) and 2,2′-biquinoline-4,4′-dicarboxylic acid dipotassium salt (BQC) modifiers of $PdCl_2$ precursors the catalytic

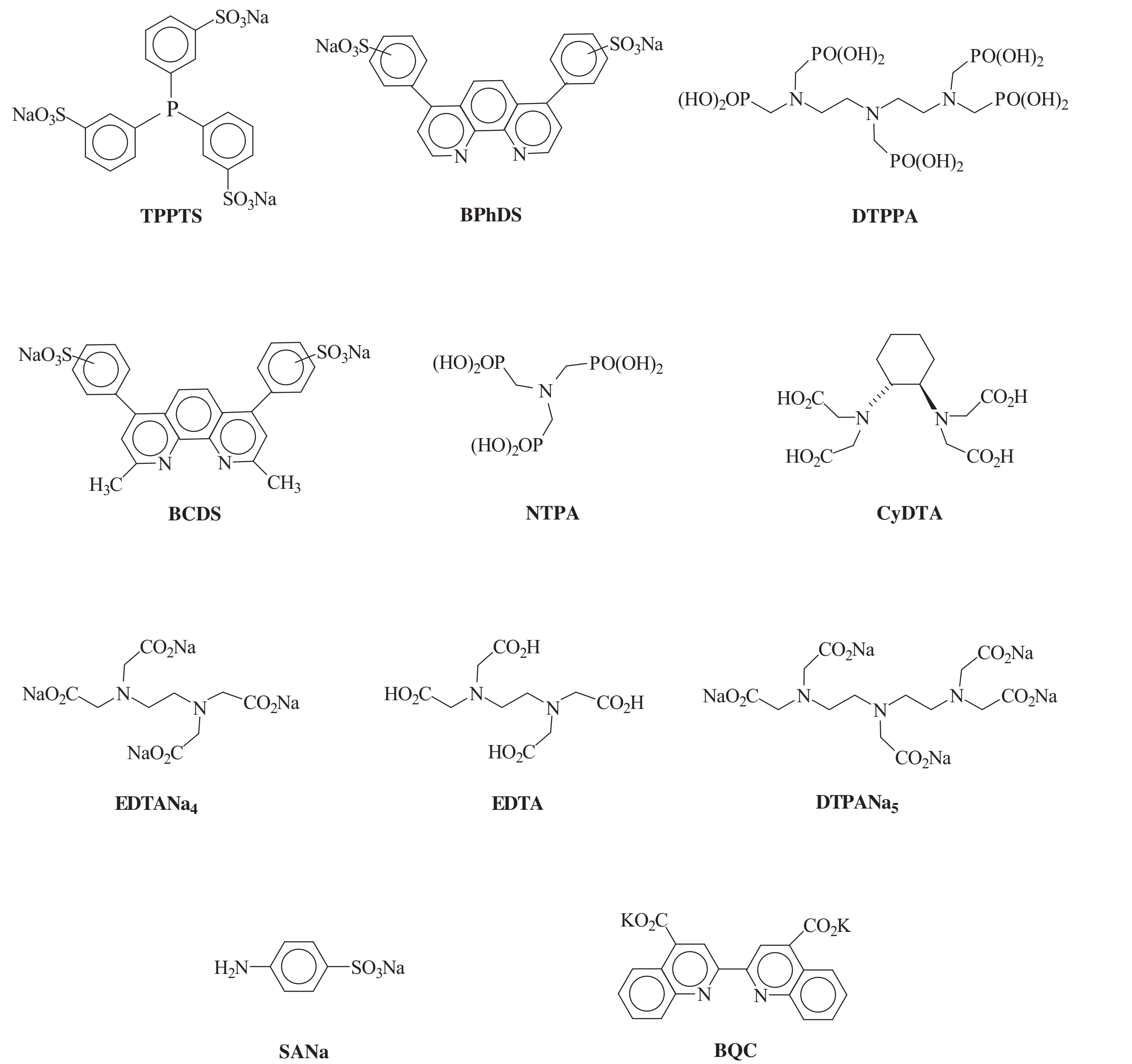


Fig. 1. Structures of the water-soluble ligands triphenylphosphinetrisulfonic acid trisodium salt (TPPTS), bathophenanthrolinedisulfonic acid disodium salt (BPhDS), diethylenetriaminepentakis(methylphosphonic acid) (DTPPA), bathocuproinedisulfonic acid disodium salt (BCDS), nitrilotris(methylphosphonic acid) (NTPA), trans-1,2-diaminocyclohexane-N,N,N′,N′-tetraacetic acid (CyDTA), ethylenediaminetetraacetic acid tetrasodium salt ($EDTANa_4$), ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid pentasodium salt ($DTPANa_5$), sulfanilic acid sodium salt (SANa) and 2,2′-biquinoline-4,4′-dicarboxylic acid dipotassium salt (BQC).

hydrogenation activities obtained were lower from 39,700 up to 44,100 TOF's per hour (Table 2, entries 2/11–2/13) which are still higher than the catalytic activity (TOF = 34,500 h^{-1}) exhibited by $PdCl_2$/TPPTS catalyst (Table 1, entry 1/11). An exceptionally high catalytic activity of TOF = 110,000 h^{-1} was achieved by a water-soluble palladium catalytic complex containing nitrogen ligands namely the $PdCl_2$/BPhDS catalyst in the partial hydrogenation reaction of MESBO at a molar ratio of C=C units/Pd = 15,000 and BPhDS/Pd = 1, a reaction temperature of 120 °C under 20 bar hydrogen partial pressure within 3 min of reaction time and a palladium concentration of only 35 ppm in water with a volume ratio of aqueous/organic phase = 1.46 without addition of any organic solvents in aqueous/organic two-phase systems (Table 2, entry 2/14).

After the reaction small amounts of palladium black particles were observed in all biphasic hydrogenation reactions in the presence of in situ formed catalysts from palladium precursors with nitrogen ligands (Table 2).

3.1.3. On the nature of water-soluble palladium catalysts containing nitrogen ligands in the hydrogenation of MESBO, mercury poisoning, dynamic light scattering and recycling experiments

The water-soluble palladium catalysts containing nitrogen ligands used in this work (Table 2) was prepared in situ after dissolution under argon of palladium precursor with the nitrogen-containing ligand in H_2O and immediate subjection of the mixture

to a hydrogen atmosphere under the chosen hydrogenation reaction conditions.

The absence of an induction period in the MESBO biphasic hydrogenation might suggest for a homogeneous nature of the catalyst and not to the presence of palladium catalytic nanoparticles [51].

In order to verify whether the MESBO biphasic hydrogenation reaction proceeds homogeneously by Pd/BPhDS catalytic complexes in water we tested this catalyst by means of mercury poisoning experiments. Mercury is a well-known heterogeneous catalyst poison because of its adsorption onto the surface of transition metal(0) catalysts or due to amalgam formation and it is probably most effective in poisoning metals that form an amalgam like the palladium(0) metal [51–54]. A large excess of Hg(0) which is 300 equiv. over the Pd/BPhDS catalyst was added to the aqueous catalyst solution and the biphasic MESBO hydrogenation reaction was performed according to the conditions described in entry 3/6 of Table 3. The addition of mercury(0) to the biphasic hydrogenation reaction mixture (Table 3, entry 3/6) results in significantly reduced TOF's of only 60 per hour compared with the catalytic activity of 3100 TOF's per hour obtained in the absence of Hg(0) under the same reaction conditions (Table 3, entry 3/5) which suggests that mercury has inactivated the catalyst. This result provides a good evidence of the presence of heterogeneous palladium(0) catalytic nanoparticles.

Dynamic light scattering (DLS) experiments on an aqueous catalyst solution with in situ formed catalyst from $[Pd(OAc)_2]_3$ with BPhDS and on an aqueous catalyst solution with a preformed $PdCl_2$/BPhDS catalyst which was recycled after a consecutive biphasic MESBO hydrogenation reaction evidenced the presence of micelles with an average hydrodynamic radius of 36 nm with in situ formed $[Pd(OAc)_2]_3$/BPhDS catalyst and an average hydrodynamic radius of 57 nm with preformed and recycled $PdCl_2$/BPhDS catalyst. These DLS measurements also evidenced that the hydrodynamic radius of micelles has been influenced by the size of the counter anion of the palladium catalyst precursor in the following order: $Cl^- > CH_3COO^-$. The group of A. Roucoux [55,56] has evidenced with DLS measurements the effect of the influence of counter anion of cationic surfactants used as protective agents for rhodium(0) catalytic nanoparticles on the hydrodynamic radius of the micelles in asymmetric hydrogenation reactions in aqueous media.

A recycling experiment with a consecutive run was carried out in the hydrogenation of MESBO in order to prove the stability of preformed Pd/BPhDS catalysts in aqueous/organic two-phase systems (Table 3, entries 3/1 and 3/2). 0.89 mg (0.005 mmol) $PdCl_2$ and 2.68 mg (0.005 mmol) BPhDS were added to 15 ml of demineralized H_2O and after slight heating for a few minutes the mixture was stirred overnight at room temperature to give a clear pink-yellow solution. The amount of uncomplexed palladium was then removed by filtration. The aqueous solution of preformed Pd/BPhDS catalyst was charged with 13.01 g (60 mmol of C=C units) of MESBO 3 mixture into an Autoclave Engineers autoclave (100 ml) which was equipped with a stir bar driven by an IKA magnetic stirrer (poorer mixing) because its own MagneDrive III agitator system was out of order. In the reaction mixture the molar ratio of C=C units/Pd was 12,000. After a number of pressurizing–depressurizing cycles with hydrogen to remove last traces of air oxygen, the autoclave was pressurized and contents were heated with stirring. The heating time to reach a reaction temperature of 120 °C was 4 min. At the reaction temperature of 120 °C the hydrogen partial pressure was 20 bar and the reaction time 20 min. After the reaction the autoclave was cooled (within 3 min) to room temperature, vented of hydrogen and the reaction mixture removed. After the reaction the Pd/BPhDS catalyst was easily recovered by a simple phase separation of the aqueous phase which has a black-brown colour from the upper organic layer and the aqueous phase containing the

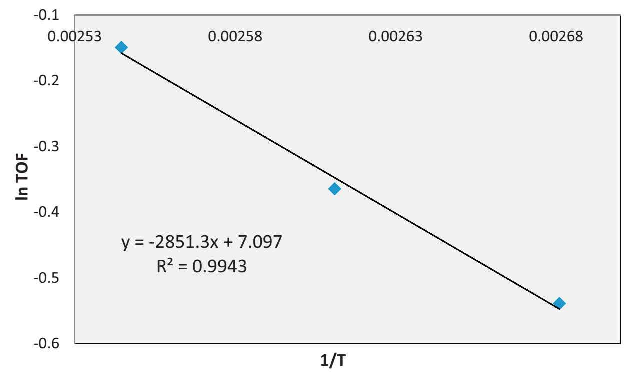


Fig. 2. Calculation of the apparent Arrhenius parameter of the activation energy.

catalyst after separation of a minor amount of palladium black was re-used under the same hydrogenation reaction conditions after addition of a new portion of 13.01 g (60 mmol of C=C units) of MESBO 3 mixture. After the recycling hydrogenation experiment a minor amount of palladium black formation was observed and the pH value of the aqueous catalyst solution was 3.56. The catalytic activity remained almost unchanged high (TOF = 5480 h^{-1}) using the recycled Pd/BPhDS catalyst in the biphasic hydrogenation experiment of entry 3/2 compared with the first biphasic reaction of entry 3/1 using the preformed Pd/BPhDS catalyst (TOF = 5400 h^{-1}). This recycling experiment of the partial hydrogenation of MESBO at 120 °C catalyzed by heterogeneous palladium(0) nanoparticle catalyst stabilized by BPhDS in micellar systems in aqueous media with unchanged activity in a consecutive run also at 120 °C indicates a stable palladium(0) catalytic nanoparticle system which is even more remarkable when one considers that transition metal(0) catalytic nanoparticles are usually applied at much lower temperatures due to usually their lower stabilities. Dynamic light scattering measurements on the aqueous Pd/BPhDS catalyst solution obtained after the recycling hydrogenation experiment of entry 3/2 evidenced the presence of micelles with an average hydrodynamic radius of 57 nm.

In order to calculate the apparent Arrhenius parameter of the activation energy, the hydrogenation reaction of MESBO catalyzed by palladium(0) nanoparticles stabilized by BPhDS in micellar systems was carried out at 100, 110 and 120 °C and the obtained results are summarized in Table 3, entries 3/3–3/5. The apparent activation energy which was calculated with these data (Fig. 2) amounts to 23.7 kJ/mol. This result is of the same order of magnitude (35 kJ/mol) as reported earlier for palladium(0) catalytic nanoparticles stabilized by dendritic core-multishell architectures applied in hydrogenation reactions [57]. The rather low apparent activation energy of 23.7 kJ/mol indicates for the presence of a very active palladium(0) nanoparticle catalyst and might suggest that the reaction rates are limited by finite rates of mass transfer probably of the organic MESBO starting material in the highly polar aqueous medium. However, the presence of micellar nanoreactors (vide infra) lowers the mass transfer barrier and thus considerably increases the rates of the catalytic hydrogenation reaction.

Transition metal(0) catalytic nanoparticles [58,59] stabilized with nitrogen- and phosphorous-containing ligands [60–62] have been applied in a broad spectrum of catalytic reactions. According to A. Roucoux [55,56,58,63] "*. . .stabilization of finely dispersed metallic particles in neat water by hydrosoluble protective agents is an original catalytic approach to prevent aggregation and to facilitate recycling. . .*" and stabilized water-dispersible transition metal(0) catalytic nanoparticles have been applied in several catalytic reactions in aqueous media [58,64]. The water-soluble ligand BPhDS has been used by Schmid et al. [65] to stabilize platinum clusters.

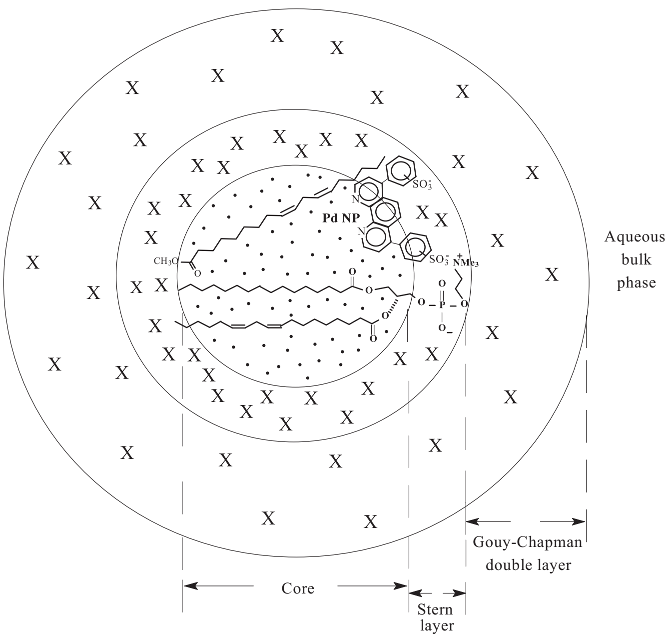


Fig. 3. Representation of a simplified proposed model of a spherical Hartley ionic micelle containing the palladium(0) nanoparticle (PdNP) catalyst stabilized by a BPhDS ligand, the zwitterionic phospholipid surfactant lecithin (phosphatidylcholine) and the starting material ML. The hydrophobic tails of lecithin and of ML in the core of the micelle (stippled part), the hydrophilic heads (NMe_3^+) interacted with the SO_3^- groups of the BPhDS ligand stabilizer in the Stern layer, the hydrophilic groups of ML in the Stern layer and Gouy-Chapman double layer, the counter ions (Na^+ and Cl^- depicted as X) schematically indicate their relative locations and not the relationship to their molecular size, distribution, number or configuration.

Very recently, Caporali et al. [66] reported on water-dispersible palladium(0) catalytic nanoparticles stabilized by a known water-soluble P,N ligand namely 1,3,5-triaza-7-phosphaadamantane and applied as catalysts in hydrogenation reactions in aqueous/organic two-phase systems.

The exceptionally high catalytic hydrogenation activities achieved by water-dispersible palladium(0) nanoparticle catalysts stabilized by water-soluble nitrogen-containing ligands in aqueous/organic micellar systems were rationalized by assuming that the stabilization mechanism of the catalytic active palladium(0) nanoparticle (PdNP) is coordinative stabilization by nitrogen ligands in the highly polar aqueous solvent and the catalytic activity is enormously increased due to the presence of micellar nanoreactors as proposed in Fig. 3. Moreover, the zwitterionic surfactant lecithin probably contributes with electrosteric stabilization and furthermore aqueous solvent molecules stabilize the PdNP catalytic system. There are four widely accepted stabilization mechanisms of transition metal(0) catalytic nanoparticles which were first introduced by Roucoux et al. [58] and include electrostatic, steric, electrosteric and coordinative stabilization by a ligand or a solvent [64]. The micelle core of Fig. 3 is composed of the hydrophobic chain of the zwitterionic phospholipid surfactant lecithin where the hydrophobic tail of ML with the C=C unsaturation units are located. Surrounding the core is the Stern layer where the charged head groups NMe_3^+ and SO_3^- of the phospholipid surfactant lecithin and BPhDS, respectively, are located together with the polar ester group of ML along with the counter ions (Cl^- and Na^+) of the ionic micelle. The PdNP catalyst is probably located on the polarity gradient between the Stern layer and the micelle core. It should also be mentioned that the catalytic hydrogenation reaction may proceed in "wet micelles" which are water-permeated micelles and water molecules are present within the micelle core [1,67].

4. Conclusions

The work presented in this paper demonstrated again the enormous high potential of environmentally friendly and sustainable aqueous-phase catalysis through efficient novel water-dispersible palladium(0) nanoparticle hydrogenation catalysts stabilized by nitrogen-containing ligands which possess even higher activities than the activity exhibited by water-soluble Pd/TPPTS benchmark catalysts in micellar nanoreactors. Great advantages of the novel biphasic hydrogenation reaction by palladium(0) catalytic nanoparticles stabilized by nitrogen-containing ligands in micelles in water are their lower price, their higher stability and furthermore that they offer the possibility of the easy and quantitative recovery of the palladium(0) catalytic nanoparticles stabilized by nitrogen-containing ligands in water in active form from the organic reaction products by a simple separation of the two phases. The water-soluble nitrogen-containing ligands with the zwitterionic phospholipid surfactant lecithin inherent in the renewable MESBO starting material in the aqueous micellar medium are efficient protective agents of palladium(0) catalytic nanoparticles to prevent aggregation and facilitate recycling of the catalyst. Hence, we are currently investigating the scope of this useful hydrogenation reaction catalyzed by palladium(0) catalytic nanoparticles stabilized by nitrogen-containing ligands in aqueous/organic micellar systems.

Acknowledgments

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